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# Order and Domain Strengthening in Highly Pure and Commercial $Cu_2NiZn$

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Vickers microhardness measurements are performed on the ordering alloy $Cu_2NiZn$ to determine the dependence of the strength upon the quench temperature and the antiphase domain size. The influence of impurities on the strength is investigated by performing the measurements on a highly pure and on a commercial alloy. A maximum in strength as a function of the quench temperature has been found, which is similar of shape and position as reported for $Ni_3Mn$. The extent of domain hardening in $Cu_2NiZn$ is rather small, like in $Ni_3Mn$ and $Ni_3Fe$. $Cu_2NiZn$, as an alloy with an $L1_2$ structure, can best be compared with $Ni_3Fe$ and $Ni_3Mn$ in its mechanical behavior, instead of with $Cu_3Au$. Transmission electron microscopy has revealed that antiphase domain growth in $Cu_2NiZn$ obeys a $D^n - D_0^n = kt$ law, where n decreases with increasing temperature, except near the critical temperature $T_{c1}$, where the antiphase boundaries align themselves along {100} planes.

PREVIOUS investigations on the relation between the mechanical properties of alloys with an $L1_2$ structure and their state of order have mostly been concerned with $Cu_3Au$. An excellent review on this subject is published by Stoloff and Davies.[1] Already in 1955 Ardley[2] performed experiments on $Cu_3Au$ single crystals and scrutinized separately the consequences of varying the antiphase domain size and the degree of order. Marcinkowski and Miller[3] investigated the change in yield and flow stress with quench temperature and the change in flow stress with aging time for different ordering temperatures on $Ni_3Mn$ polycrystalline wires. Davies and Stoloff[4] have performed Vickers hardness measurements on $Cu_3Au$ and several Ni-Fe and Ni-Mn alloys close to stoichiometric $Ni_3X$ to determine the isothermal hardening curves. More recently Calvayrac and Fayard[5] carried out tensile tests on $Ni_3Fe$ in which they determined the yield and flow stress as a function of the annealing time at a temperature just below the critical temperature.

The main conclusions that can be drawn from these investigations are:

1) If the long-range order parameter decreases, the flow stress increases (provided that the domain size is kept large). The increment is much larger for $Cu_3Au$ than for $Ni_3Mn$.

2) Close to the critical temperature the flow stress falls sharply to a value corresponding to the short-range ordered structure. For $Cu_3Au$ this decrease occurs at the critical temperature, for $Ni_3Mn$ about 15 K below it.

3) If the domain size increases, the room temperature flow stress passes through a maximum at a domain diameter of about 3 nm. Calvayrac and Fayard, however, claim that the maximum in flow stress for $Ni_3Fe$ is attained at a domain diameter of about 11 nm. Beyond the maximum softening occurs as a result of domain growth.[6] The extent of this softening process is much larger in $Cu_3Au$ than in $Ni_3Mn$ or $Ni_3Fe$.

The aim of this research is to determine the Vickers microhardness of $Cu_2NiZn$ as a function of the degree of long-range order and the average domain size. The influence of impurities on the state of order is studied by performing the measurements on highly pure $Cu_2NiZn$ and on commercial $Cu_2NiZn$.

The interpretation of the mechanical properties of $L1_2$ alloys is still a controversial matter. As Calvayrac and Fayard[5] already stated, the behavior of $Cu_3Au$ is too often extrapolated to all the $L1_2$ alloys. Therefore the experimental data on $Cu_2NiZn$ will elucidate some of the general behavior of $L1_2$ alloys.

At high temperature $Cu_2NiZn$ possesses an f.c.c. disordered structure. Below the first critical temperature, $T_{c1} \approx 774$ K for the stoichiometric alloy, a modified $L1_2$ structure exists, in which the Zn atoms occupy one of the four interpenetrating simple cubic sublattices, while the Cu and Ni atoms are still randomly distributed over the remaining three sublattices. Below a second critical temperature, $T_{c2} \approx 600$ K, a modified $L1_0$ structure exists, in which Cu occupies two sublattices and Ni the remaining sublattice.[7]

## EXPERIMENTAL

The highly pure alloy was made by melting together appropriate amounts of 5*N* copper, 4*N* nickel and 5*N* zinc in an evacuated tube of fused quartz. The alloy was homogenized at 1120 K for 10 days and subsequently cold-worked to bars of $4 \times 4 \times 15$ mm$^3$. These samples were annealed at 1120 K for 5 days in evacuated tubes of fused quartz to remove internal stresses and to obtain a large grain size. The commercial alloy was kindly provided by Wieland-Metallwerke, Ulm (FRG). Chemical analyses result in a composition of 51.6 at. pct Cu, 24.7 at. pct Ni and 23.7 at. pct Zn for the highly pure alloy and 49.7 at. pct Cu, 25.0 at. pct Ni and 25.3 at. pct Zn for the commercial alloy, with main impurities: 0.013 at. pct Mn and 0.008 at. pct Fe.

The bars were annealed in evacuated tubes of Pyrex

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glass at 830 K and quenched in water to maintain the disordered structure. Bars for investigating the microhardness as a function of the quench temperature were annealed at 723 K for 96 h to obtain a large domain size (about 105 nm) and were also quenched in water. Subsequent annealing treatments at appropriate temperatures were done in the same way. The annealing time varied from three hours for high temperature to two hundred hours for low temperature treatments. The bars were embedded in a thermoplast and carefully mechanically polished with diamond paste up to a quarter of a micron and then chemically etched. The Vickers microhardness was determined by taking the average of 24 independent indentations for the highly pure alloy and 36 independent indentations for two commercial alloys each. The average size of the grains is 200 $\mu$m and 100 $\mu$m, respectively for the two types of alloys compared with an indentation of about 40 $\mu$m in size.

The average domain size as a function of the annealing time at several temperatures is determined by imaging the antiphase domains in the Philips EM 300 transmission electron microscope. The preparation of the specimens is done in the same way as described in Ref. (8).

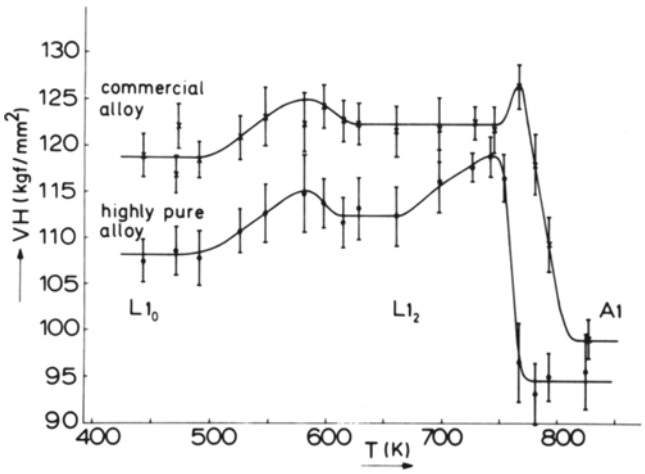


Fig. 1—Vickers microhardness *vs* the quench temperature for the highly pure and for the commercial alloy. The error bars represent the standard deviations.

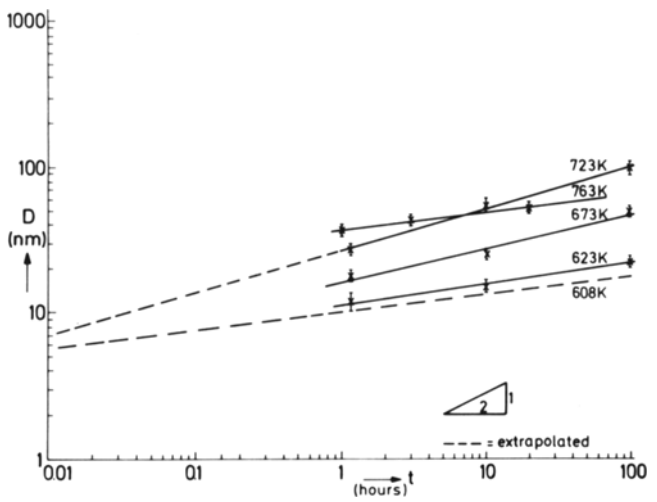


Fig. 2—Average domain size *vs* the annealing time for temperatures indicated.

## RESULTS

In Fig. 1 the relationship between the Vickers microhardness and the quench temperature is depicted both for the highly pure and for the commercial alloy. The commercial alloy has on the whole a higher microhardness than the highly pure alloy. The latter exhibits a rather strong dependence of the microhardness on the quench temperature for the $L1_2$ structure. The commercial alloy, on the contrary, shows a constancy in the temperature range of 620 K to 750 K. The maximum in the hardness of the commercial alloy lies at about 767 K, about 18 K below its critical temperature. For the highly pure alloy the maximum is situated at 750 K, about 17 K below its critical temperature which is 767 K for this composition. Taking the same temperature difference, $T_{c2}$ for the latter alloy can be estimated as 600 K. The resulting temperature range in which $L1_2$ is stable is supported by X-ray data.[7]

Figure 2 shows the relation between the average domain size and the annealing time for the temperatures: 623 K, 673 K, 723 K and 763 K. All curves obey

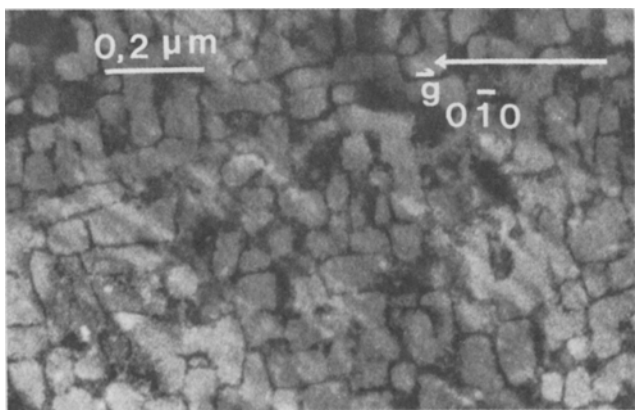


Fig. 3—Antiphase domain boundaries corresponding to a temperature of 630 K. Dark field strong beam image; projection plane (110); g = [001].

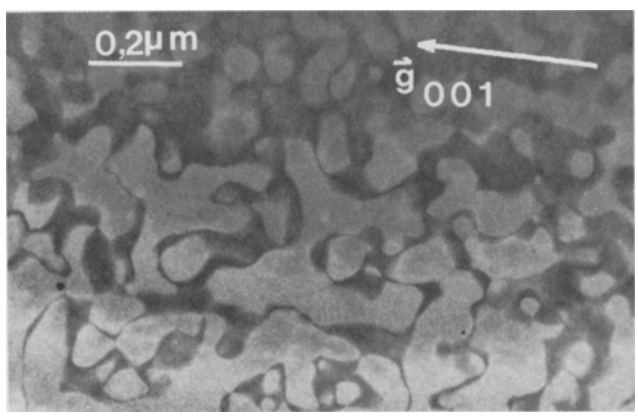


Fig. 4—Antiphase domain boundaries corresponding to a temperature of 763 K. Dark field strong beam image; projection plane (100); g = [0$\bar{1}$0].

an $D^n - D_0^n = kt$ law. In contrast to results on $Cu_3Au$ and $Ni_3Fe$, n is not equal to 2 and it is temperature dependent. As the temperature increases, n is decreasing except near $T_{c1}$, where n increases with temperature like in $Ni_3Fe$.[9] Below about 730 K the domain boundaries are curved like in $Ni_3Fe$ and $Ni_3Mn$ (Fig. 3), while above 730 K the boundaries are oriented preferentially along the cubic planes like in $Cu_3Au$ (Fig. 4). This is opposite of what one would expect, because the tendency for antiphase boundaries to align themselves along certain planes should decrease as the temperature increases.[10] The curves of 623 K, 673 K and 723 K are used to construct the curve appropriate for 608 K (dotted line). The curves of 608 K and 723 K are extrapolated to short annealing times needed for the kinetic studies in the next section. However, after the nucleation, the domain grows first at the expense of the short-range ordered matrix, a process which is much faster than the growth at a later stage, when domains are in contact with each other. This results in two linear stages as observed in $Ni_3Fe$.[5,9] The transition points in the case of $Ni_3Fe$ would occur at domain sizes smaller than 6 nm. Since the measurements are performed at annealing times corresponding to larger domain sizes, this first stage is absent in Fig. 2. Domain sizes at these short annealing times cannot be determined by means of transmission electron microscopy, because of the large experimental error involved, nor by X-ray diffraction techniques, because of the similar scattering factors.

Figure 5 shows the microhardness as a function of the $L1_2$ antiphase domain size at 723 K. The curve of the commercial alloy displays a maximum at some intermediate value of the domain size, like all other $L1_2$ alloys. The peak is situated at a domain size of about 12 nm. The highly pure alloy exhibits no maximum, and hence, only domain hardening occurs. Figure 26 shows the microhardness as a function of the $L1_2$ domain size at 608 K. The maximum is situated at a domain size of about 7.5 nm.

## DISCUSSION

Microhardness reveals the strength of a material in a rather complex manner, because it is a combination of yield strength and strain hardening. For wedge shaped indentations, the microhardness should be compared with the flow stress at 15.2 pct strain.[11] Since the strain hardening coefficient of $Cu_2NiZn$ is not known as a function of quench temperature, it is not possible to give a quantitative comparison between the experimental results of Fig. 1 and the existing theories of the yield stress for ordered alloys. Such a comparison between the experimental and theoretical yield stress as function of the long-range order parameters will be the subject of a subsequent paper.

Marcinkowski and Miller[3] measured the flow stress of $Ni_3Mn$ as a function of the quench temperature. The curve for 10 pct strain is similar to Fig. 1 with respect to position, width and height of the maximum just below $T_{c1}$ and the magnitude of the drop in microhardness relative to the $L1_2$ strength. Ardley[2] measured the yield stress of $Cu_3Au$ single crystals at temperature. He observed a maximum at the critical temperature with a relative height much larger than the one observed in Fig. 1.

Several order strengthening theories are proposed in the literature. Due to the very large domains (> 100 nm), only a very small contribution of Cottrell's domain hardening mechanism[6] is adding to the strength of the present alloys. Flinn's mechanism of antiphase boundary formation as a result of dislocation climb[10] does not apply here, because the deformation is performed at room temperature and hence no dislocation climb occurs. Brown[12] accounts for the difference in energy between the thermal equilibrium configuration of the antiphase boundary connecting the two unit dislocations of a superdislocation, and its higher energy state after shear. However, this theory cannot account for the maximum at strains as large as 10 pct, since at these high strains most of the initially pinned dislocations will be free from their thermal equilibrium antiphase boundaries, so no maximum should occur. None of these strengthening mechanisms can account for the observed microhardness as a function of the quench temperature. Sumino[13] argued that the stress field of the dislocations causes oriented short-range order resulting in a maximum strength at the critical temperature. However, the maximum strength is observed 18 K below the critical temperature (like in $Ni_3Mn$) in disagreement with Sumino's theory. Marcinkowski and Miller explained their results on $Ni_3Mn$ with short-range order strength-

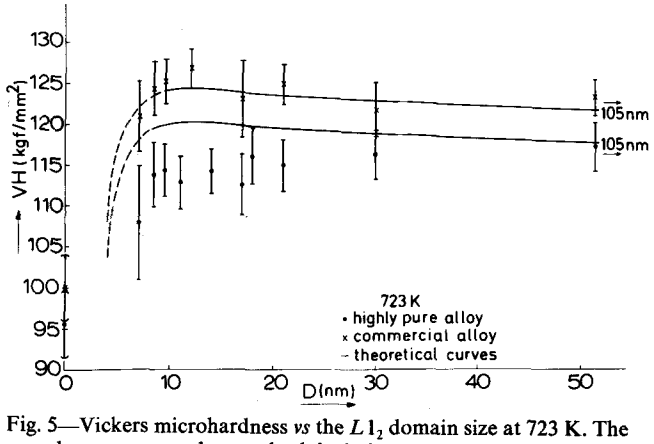


Fig. 5—Vickers microhardness *vs* the $L1_2$ domain size at 723 K. The error bars represent the standard deviations.

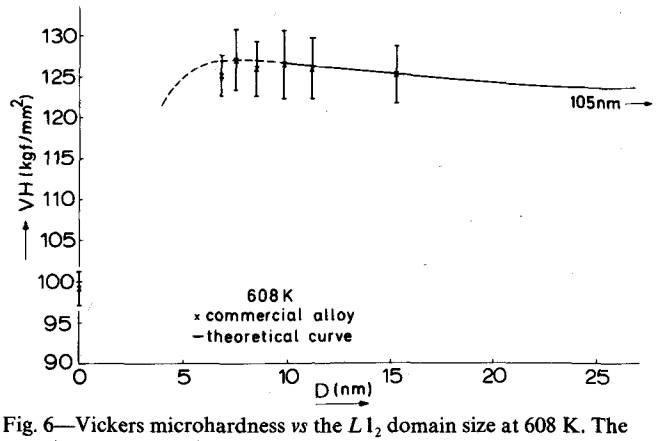


Fig. 6—Vickers microhardness *vs* the $L1_2$ domain size at 608 K. The error bars represent the standard deviations.

ening, based on the work of Fisher[14] and Rudman.[15] Nearest neighbor short-range order and long-range order parameters calculated[16] within the tetrahedron approximation of the Cluster Variation Method of Kikuchi for $Cu_2NiZn$ are used to determine the short-range order strengthening as proposed by Fisher and Rudman. No significant strengthening was calculated for the ordered alloy, so this mechanism is not likely to be predominant. Davies and Stoloff[17] suggested that a transition of superdislocation to single dislocation motion occurs at the critical temperature. Cook[18] and Moine[19] developed this suggestion into a quantitative description of the yield strength as a function of the order parameters. For $Cu_2NiZn$ these theories result in a yield stress for the disordered alloy much lower than for the ordered alloy. Preliminary tensile measurements on both types of alloys, however, indicate that the yield stress is about the same for the ordered and disordered alloy. As a matter of fact, the yield stress measured is 120 MPa for a commercial alloy and 110 MPa for the highly pure alloy. Moreover, the strain hardening coefficient for both alloys is 1180 MPa and 830 MPa for the ordered and for the disordered alloys, respectively. We now express the Vickers hardness as a function of the flow stress according to the equation:[11]

$$VH = C \cdot [\sigma_Y + 0.152 \cdot \theta_{II}], \qquad [1]$$

where $\sigma_Y$ is the yield strength and $\theta_{II}$ is the strain hardening coefficient. The proportionality coefficient C calculated from the mechanical properties of the disordered alloys is 0.406 for both alloys. The Vickers microhardness, calculated from the above data for the ordered alloys using the same C-value are 121 (kgf/mm$^2$) and 117 (kgf/mm$^2$), respectively, which is in good agreement with the observed values. The strong dependence of the microhardness on the quench temperature close to $T_{c1}$ in Fig. 1 and the absence of a maximum in the annealing curve of Fig. 5 for the highly pure alloy can be explained by its composition. The alloy is not stoichiometric and therefore possesses a two phase structure close to $T_{c1}$.

The maximum in the annealing curves of Figs. 5 and 6 should be due to the transition from single dislocation slip to superdislocation slip,[4] as was observed by electron microscopy in the case of $Ni_3Fe$ and $Ni_3Mn$.[5,20] At small domain sizes, when slip takes place by the movement of unit dislocations, short-range order strengthening as proposed by Fisher[14] occurs. Just before the maximum a two phase structure of ordered domains in a short-range ordered matrix exist.[4,5] The superdislocations will move easily through the ordered domains but require extra stress to move through the matrix as they decrease the short-range order.[3] At the maximum a contiguous domain structure is present, so Cottrell's domain strengthening mechanism applies:

$$\tau = \frac{\gamma}{D}\left(1 - \frac{\alpha t}{D}\right), \qquad [2]$$

where $\tau$ is the critical resolved shear stress, $\gamma$ is the antiphase boundary energy, $D$ is the average domain size, $\alpha$ is a geometrical factor, being 6 for cubic domains and 3 for spherical domains and $t$ is the thickness of the domain boundary.[6] Since the microhardness is measured as an average over many grains, the shear stress in Eq. [2] should be multiplied by the Taylor factor $m$. For very large domain sizes no domain hardening occurs, the microhardness then being proportional to the flow stress at 15.2 pct strain. Assuming that these two contributions (Eq. [1] and Eq. [2]) to the strength are additive, the microhardness can be written as:

$$VH = C\left[\frac{m\gamma}{D}\left(1 - \frac{\alpha t}{D}\right) + (\sigma_Y + 0.152 \cdot \theta_{II})\right], \qquad [3]$$

where $VH$ is the Vickers microhardness in kgf/mm$^2$, $C$ is the proportionality coefficient, $\sigma_Y$ is the yield strength of the ordered alloy in MPa for very large domain sizes and $\theta_{II}$ is the strain hardening coefficient of the ordered alloy in MPa. Equation [3] results in a maximum at a domain size of 2 $\alpha$t, which is obtained from Figs. 5 and 6. The antiphase boundary energy has been calculated using theoretical ordering energies and long-range order parameters[21] resulting in the values 0.080 (J/m$^2$) at 723 K and 0.084 (J/m$^2$) at 608 K. Since all parameters in Eq. [3] are known, theoretical curves of the microhardness as a function of the average domain size can be computed. They are displayed in Figs. 5 and 6 as solid lines. Equation [3] only applies when a contiguous domain structure is present. The left part of the calculated curves are therefore shown as dotted lines. The experimental values agree very well as far as the commercial alloy is concerned. However, for the highly pure alloy less agreement is obtained, probably due to a non-stoichiometric composition, resulting in a two phase structure of ordered domains in a short-range ordered matrix. Taking $\alpha$ equal to 4, the antiphase domain boundary thickness t is 1.4 nm at 723 K and 0.9 nm at 608 K, which is smaller than observed in transmission electron microscopy (Figs. 3 and 4).

On comparison with the strength at infinite domain size, the contribution of the domain hardening to the total strength of the alloys is 4 pct at the maximum and 1 pct at a domain size of 100 nm, as can be seen in Figs. 5 and 6. According to Ardley[2] the domain hardening in $Cu_3Au$ amounts to 55 pct of the total strength at 598 K, where as for $Ni_3Fe$ and $Ni_3Mn$ alloys this value is about 5 pct.[4]

## CONCLUSION

From this work the following conclusions can be drawn:

1) The maximum in strength as a function of the quench temperature is situated at about 18 K below the critical temperature, like in $Ni_3Mn$. The width and the height of the maximum and the drop in microhardness after the maximum is similar to the curve of the flow stress as a function of the quench temperature for 10 pct strain of $Ni_3Mn$.[3]

2) The theories of Brown, Flinn and Rudman cannot account for the observed dependence of the microhardness on the quench temperature in the case of $Cu_2NiZn$.

3) Antiphase domain growth in $Cu_2NiZn$ obey a $D^n - D_0^n = kt$ law, where n decreases with increasing temperature, except near $T_{c1}$, where the antiphase

boundaries align themselves along {100} planes.

4) The extent of domain hardening in $Cu_2NiZn$ is small, like in $Ni_3Mn$ and $Ni_3Fe$.[4] The opposite is true for $Cu_3Au$.[2]

5) $Cu_2NiZn$, as an alloy with an $L1_2$ structure, can best be compared with $Ni_3Mn$ and $Ni_3Fe$ as regards its mechanical behavior, instead of with $Cu_3Au$.

## ACKNOWLEDGMENTS

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